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On Paranitroorthotolylphenylsulphone and Some of its Derivatives.

A Dissertation Submitted to the Board of University Studies of the Johns Hopkins University for the Degree of Doctor of Philosophy.

By

Robert Stewart Norris.

1897.

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On Paranitrothiotolylphosphinsulfochloride and Some of Its Derivatives.

Introduction.

In a series of investigations carried on in this laboratory on derivatives of orthosulfobenzoic acid, it has been shown that when its potassium salt is treated with phosphorus pentachloride two isomeric chlorides are formed,[1] the formulas of which have been determined to be, $C_6H_4<^{COCl}_{SO_2Cl}$ and $C_6H_4<^{CO-O}_{SO_2}>P$.

On treating either of these chlorides with aluminum chloride and benzene, one of

[1] Remsen and Dohme, Am. Chem. Jour., 11, 141.
Remsen et al, Am. Chem. Jour. 17, 604; 18, 776.

the chlorine atoms is replaced by a phenyl group; and the products formed in both cases were identical.[1] There must, therefore, be a rearrangement of the grouping of the atoms in one of the reactions.

There are three possible formulas for the product, $C_6H_4\langle^{CO}_{SO_2}\rangle C_6H_5$, $C_6H_4\langle^{COC_6H_5}_{SO_2}\rangle$, $C_6H_4\langle^{C_6H_5}_{SO_2}\rangle C_6H_5$

I. II. III.

From its properties and reactions the most probable structure seems to be that represented by the second formula, the phenyl residue being in combination with a carbonyl group. Since on

[1] Fenton and Saunders, this Journal

and Saunders[1] converted the chloride into the corresponding sulphonic acid by replacing the chlorine with a hydroxyl group; prepared a number of derivatives from this; and studied their properties. They also obtained a diphenyl derivative of orthosulphobenzoic acid, of the formula, $C_6H_4 \begin{cases} CO.C_6H_5 \\ SO_2.C_6H_5 \end{cases}$, by the more prolonged action of benzene and aluminium chloride on the dichloride. The arguments which they bring forward in favor of the structure represented by the formula $C_6H_4 \begin{cases} CO.C_6H_5 \\ SO_2.Cl \end{cases}$ for the first-

[1] Loc. cit.

product of the reaction are,[1]
1. That the acid formed by the decomposition of the chloride with water is a very soluble substance, and difficult to obtain in a crystalline form.

This is ~~my~~ characteristic of sulphonic acids in general, while, on the other hand, the corresponding carboxyl acids are much less soluble, and easily obtainable in the form of crystals. Sarcophenylsulphonic acid, for instance, $C_6H_4 \begin{cases} SO_3H \\ CO.NH_2 \end{cases}$ (4), described by Hewett,[2] is a difficultly soluble, crystalline compound; and another example will be described later in this paper.

1 Remsen and Saunders, Am. Ch. J., [illegible].

2 Hewett, Diss., Johns Hopkins University, 1892.

2. That the decomposition of the potassium salt by fusion with caustic potash gives benzoic acid and benzene sulphonic acid.

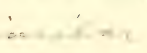
It is true, that on purely theoretical grounds this might be a possible reaction with either of the substances represented by the formulas, —

$C_6H_4 \begin{cases} CO_2H \\ SO_2OK \end{cases}$ and $C_6H_4 \begin{cases} COOK \\ SO_2OH \end{cases}$

I. II.

But when we come to consider the experimental evidence on the point it seems much more probable that these products would result from a compound having the first formula, than one having the second. Hübner

sulphone, for instance, when fused with caustic potash breaks down completely into diphenyl, sulphur dioxide, and phenol, and various other substances. Polysulphones in a similar manner.[2] And these reactions take place with difficulty, showing the stability of the sulphone grouping.—



The way in which the diphenyl-substitution-product of ortho sulphobenzoic acid breaks down also furnishes evidence in favor of this view. They found that it decomposes readily under similar circumstances into benzoic

1 Otto, Ber. d. chem. Ges. 19, 2242

2 Otto, Ber. [illegible]

and and diphenyl sulphone,

$C_6H_4 < \begin{matrix} CO\,C_6H_5 \\ SO_2\,C_6H_5 \end{matrix} + H_2O = C_6H_4 < \begin{matrix} SO_2\,C_6H_5 \\ CO_2H \end{matrix} + C_6H_6$

2. That the alkyl ether breaks down very readily on standing in contact with alcohol, into the acid; which points to its being an ester of a sulphonic acid rather than of a carbonic acid.

3. That the chloride on treatment with ammonia, instead of forming an amide, goes into the lactim condition. This is in accordance with the supposition that the chlorine atom left in the molecule is that one united with the carbonyl group.

The evidence, therefore,

pretty clear, that of the two formulas $C_6H_3 < \overset{Cl}{\underset{SO_2Cl}{}} \overset{NO_2}{}$ and $C_6H_3 < \overset{NO_2}{\underset{SO_2Cl}{}} \overset{Cl}{}$, the former is the more probable for the compound obtained from the isomeric chlorides of orthonitrophenylsulphuric acid by the Friedel and Crafts reaction with benzene.

Paranitrorthosulphobenzoic acid had also been found to yield two isomeric chlorides[1] by treatment with phosphorus pentachloride,

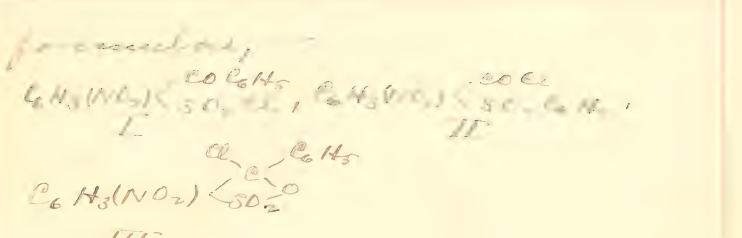
$C_6H_3(NO_2) < \overset{COCl}{\underset{SO_2Cl}{}}$ and $C_6H_3(NO_2) < \overset{CO}{\underset{SO_2}{}} > O$

These in turn yield the same phenyl substitution-product, when treated with benzene and aluminium chloride,[2] leaving the three possible

1) Gray, Inaug. Diss. Johns Hopkins University, 1888.

2) Hollis, Inaug. Diss. Johns Hopkins University, 1890.

formulæ,



I. II.

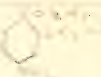
III.

But the reaction seems in this case to stop here, — no diphenyl substitution-product is formed by the further action of the reagents.

The same question arises in this case as in that of the compound just discussed. Which of the chlorine atoms is replaced by the phenyl groups? Hollis[1] investigated the product formed, and found from its properties and reactions somewhat similar conclusions

[1] See note

in favor of the former formula as that found by Remsen and Saunders in the former case. The acid obtained by decomposing the chloride with water or acids was very soluble, and could not be obtained in the form of crystals. The ethyl ether of the acid was found to be so unstable, if one exists at all, as to pass over immediately into the acid, when an attempt was made to prepare it from the chloride and absolute alcohol. On treating the chloride with ammonia a reaction was formed. These three reactions are perfectly analogous to those which take place with benzoyl chloride and phosphorus chloride under similar conditions.

and point to the structure,

for the chloride. But the most conclusive evidence obtained by Remsen and Saunders for the formula which they gave, namely the products formed by the decomposition of the chloride on fusing with caustic potash, was not duplicated in the present case. The presence of the nitro group would probably make such a test less satisfactory. The evidence in this case is not as convincing as it is in that of the more simple compound.

There is, however, another method of attacking the problem, by which just as conclusive evidence, but of a different

kind might be obtained. It was for the purpose of determining the evidence of this evidence that the present investigation was undertaken.

If a compound with the formula could be prepared, and its properties should be different from that obtained by Noelting from the isomeric chlorides of paranitro- or thiosulphobenzoic acid, the latter could not have the same structure, and therefore probably have the formula . If their properties should be the same, the structure of the two would, of course, be identical.

The best method of

suggested itself for preparing
paranitrorthophenylsulphon-
carboxyl chloride was to start
with paranitrotoluene,
convert it into paranitrotolu-
orthosulphonic acid by treatment
with fuming sulphuric acid,
treat the potassium salt of this
with phosphorous pentachloride
to form paranitrotoluenorthe-
sulphon chloride, from which
paranitrotoluenorthophenyl-
sulphone could be made by the
Friedel and Crafts reaction
with benzene. By oxidation of the
methyl groups, paranitrorthe-
phenylsulphonebenzoic acid
would be formed, and this
could be transformed into

paranitrobenzenesulphon-
dimethylchloride by the action
of phosphorous pentachloride.
The previous necessity for such
a long series of transformations,
in case they all took place, was
an abundance of material
to start with, in order that
the end product might be
obtained in sufficient quantity
for investigation should the
yields obtained at different
stages be small.

Another method was tried,
starting from paranitrobenzene-
orthosulphonic acid $C_6H_3(NO_2)(SO_3H)$
This was to be converted into
the chloride $C_6H_3(NO_2)<\overset{Cl}{SO_2Cl}$, and
the chlorine then replaced by

followed, by means of the Hinsberg reaction. The tertiary amines would react to form water-soluble quaternary salts, and p-nitrobenzenesulphonyl chloride formed from this with phosphorus pentachloride, basic amines were separated by this method.

Preparation of Material.

Paranitrotoluene orthosulphonic Acid.

This acid was prepared by the method originally described by Beilstein and Kuhlberg[1], and subsequently by Mark, Kastle, Gray and others[2] in this laboratory. There are a number of important details which are not to be found mentioned in any one article and which it is necessary to observe in order to obtain a good yield, and a pure product, so it may not be out of place to give the details of the process by which these results were obtained.

Two hundred grams of

1 Ann. Chem. (Liebig) 155, 1.

2 Young, Am. Chem. Journal, [illegible]

grams paranitrotoluene were placed in a three-litre flask, and sixteen hundred grams of fuming sulphuric acid added. The fuming sulphuric acid contained in the original sealed bottles is sufficiently strong for the purpose, but acid which has been standing for any length of time in the bottle after they have once been opened has usually absorbed so much water as to be unfit for use in this preparation. The addition of sulphuric trioxide to the acid before using it is to be recommended in the bottle room.

The flask was then placed in a large water-bath so as to

be immersed in the water up to the mark, and the water heated to boiling. At intervals of fifteen to twenty minutes the solution was thoroughly agitated by shaking the flask, and after the solution had been heated for two or three hours a sample was occasionally removed from the flask and added to water to determine when the solution was complete, which was indicated by its being entirely dissolved. The time taken to completely decolorize the permanganate depends mainly on the strength of the acid, due to prevent over-oxidation by too concentrated

At the end of this time the solution was allowed to cool down to the ordinary temperature. The dark brown syrupy liquid obtained in this manner was poured into about sixteen litres of water contained in large evaporating dishes, which were not more than two thirds full. If the reaction had taken place properly the thoroughly mixed water solution should be quite clear and free from any undissolved matter. Should this not be the case the solution should be filtered. Potassium carbonate — precipitate

of chloride were then added in small portions to the acid solution until no further effervescence took place, the solution being stirred during the addition. The precipitated calcium sulphate and excess of calcium carbonate were then filtered off through a cloth filter. This did not remove all of the precipitate, so it was necessary to filter again through paper, in order to prevent the formation of a large amount of calcium potassium sulphate in the next stage of the process. The collected calcium sulphate

precipitates were then extracted with water, and the supernatant liquid decanted off through a filter, and added to the main solution, which was then heated to boiling. A solution of potassium carbonate was added until litmus paper indicated a slight alkaline reaction, and the precipitated calcium carbonate filtered off. The dark brown solution was boiled for an hour with animal charcoal, and again filtered. The removal of the animal charcoal was found to be a slow process, and was accomplished by means of a large plaited filter paper.

The use of the filter-pump with a flat filter does not hasten the process. A Witt plate covered with a small filter paper used in connection with a filter pump, and previous filtration through cloth were tried, but the fluted filter papers were found to be most expeditious. The charcoal did not remove all of the color from the solution, which was still brownish yellow. It was evaporated to one half of its original volume, and the potassium salt allowed to crystallize out over night. The solution was filtered off from

the first crop of crystals was further concentrated, more potassium acid oxydalleyed out, and so on, reducing the volume of the solution thereof equal to about two litres when it was again treated with ammoniacal chloride, filtered and evaporated down to one litre. The mother liquor left after the crystals had separated out of this solution was thrown away, and the crystals formed were dissolved from water. The crystals which separated out at different times, were drained as thoroughly as possible with the filter pump, spread out

on large sheets of paper of double thickness, which were changed occasionally for dry sheets, and kept moist through by day. On this condition they appeared as very light yellow crystals. Eighthundred and twelve grams of the dry salt were obtained from the fourhundred grams of para nitrotoluene used.

It has been shown by Limpricht[1] that the compound formed by the action of fuming sulphuric acid on paranitrotoluene is para nitro orthotoluene sulphonic acid. He converted the acid formed by this reaction, $C_6H_3\begin{cases}CH_3\\NO_2\\SO_3H\end{cases}$, into amido-

[1] Ann. Chem. (Liebig) 161, 1

toluenesulphonic acid $C_6H_3\begin{cases}CH_3\\SO_3H\\NH_2\end{cases}$ by reduction of the nitrogroup which is known to be in the para position with reference to the methyl group on account of the formation of the acid from paranitrotoluene. This was diazotised to paradiazotoluenesulphonic acid $C_6H_3\begin{cases}CH_3\\SO_3\\N\\N\end{cases}H$, which was converted into toluenesulphonic acid by boiling with absolute alcohol, according to the following reaction,—

$$C_6H_3\begin{cases}CH_3\\SO_3\\N\\N\end{cases}H + C_2H_5OH = C_6H_4\begin{cases}CH_3\\SO_3H\end{cases} + N_2 + C_2H_4O$$

On fusing this product with caustic potash, a reaction which may be represented in two stages took place,

$$C_6H_4 \begin{cases} NH_2 \\ SO_3H \end{cases} + KOH = HKSO_3 + C_6H_4 \begin{cases} NH \\ OH \end{cases}$$

$$C_6H_4 \begin{cases} CH_3 \\ OH \end{cases} + KOH + H_2O = C_6H_4 \begin{cases} COOK \\ OH \end{cases} + 3H_2.$$

And this product formed was found to be the potassium salt of salicylic acid, $-C_6H_4 \begin{cases} COOK \\ OH \end{cases}$ (2) Therefore the nitrotoluene-sulphonic acid should from what has gone for the structural formula, $C_6H_3 \begin{cases} CH_3 \\ OH \\ NO_2 \end{cases}$. And the compound obtained by the process above described is the potassium salt of paranitro-orthotoluene-sulphonic acid.

Paranitrotoluene-
sulfonic Chloride.

Jensen[1] heated the potassium salt of paranitrotoluenesulfonic acid to 140° C. and found that it did not lose in weight. It is therefore unnecessary to dehydrate the salt before treating it with phosphorus pentachloride. The method made use of in preparing the chloride was also first used by Jensen.[2] Four hundred and sixty grams of the potassium salt of paranitrotoluenesulfonic acid were treated in twenty gram portions with an equal weight of phosphorus

[1] Diss. Chem. Leipzig, 1894, 1895.
[2] Loc. cit.

pentachloride, thoroughly mixed in a mortar and placed in a small evaporating-dish over a sulphuric-acid bath. The bath was heated up, and reaction began when the temperature reached 120°-130°C., continuing at the same temperature, until completed. The mixture was kept at the same temperature for half an hour, in order to evaporate off most of the oxychloride. After allowing it to cool to the ordinary temperature, it was poured into a tall cylinder containing water at 20°-30°C. and agitated until

the water by means of a rubber disk on the end of a glass rod. The warm water keeps the chloride in a liquid state, and it can be more thoroughly washed in this condition than if solid. After allowing the chloride to settle the wash-water was decanted or siphoned off, more warm water added and the process of washing repeated. Cold water was finally added, whereupon being shaken up with which the chloride immediately solidifies. It was then ground up into a fine powder in a mortar, and washed with cold water

mantle the mass-mixture was decanted off through a filter was free from phosphoric acid. The water was drained off by means of a filter-pump, and the chloride dried with drying paper. 370 grams were obtained.

The paranitrotoluolsulphone chloride prepared in this way was a yellow powder, melting at 92-93° C., and readily soluble in ether from which it crystallized in large, rhombic crystals melting at 94° C. (uncor.). Although a number of different methods of manipulation were tried, none were found to yield as

good results on this case. The light a temperature, or heating too long decreases the yield, and makes the chloride dark. The purity of the product depends a great deal on that of the potassium nitrite used. The color of the latter was found to be carried over into the chloride.

Paranitroanthrolutein sulphone chloride has been described as a liquid.[1] The sharp melting-point of the product prepared by the above process and crystallized from chloroform evidences its purity, and the crystals are

[1] Noyes, Am. Chem. Journ., 9, 16.

of the chlorides in the liquid state at the ordinary temperature must be considered to be very improbable. A common experience in working with solid anhydrous chlorides is that the ease with which any particular specimen can be made to crystallize is very much dependent on its purity.

Dinitrotoluenesulfonyl chloride

$C_6H_3\begin{cases}CH_3 \\ SO_2Cl \\ NO_2(1) \\ NO_2(1)\end{cases}$

This was obtained from paranitrotoluenesulfonic chloride by means of the Friedel and Crafts reaction with benzene.

Limpricht[1] obtained a compound isomeric with this, by the action of chloride and toluene on metanitrotoluenesulfonic chloride,—

$C_6H_3\begin{cases}NO_2(1) \\ SO_2Cl \\ CH_3(3)\end{cases} + H]C_6H_5 = C_6H_3\begin{cases}CH_3 \\ C_6H_5 \\ NO_2\end{cases} + HCl$

the nitro and methyl groups being attached to different benzene rings. From the

[1] Ann. Chem. (Liebig), 248, 253.

properties which were ignored. It appears to be quite different from para-nitro-orthotolylphenylsulphone, except in solubility. One of these points of difference will be taken up later under the subject of the action of oxidizing agents on the sulphone.

Preparation.

As a preliminary experiment ten grams of the chloride were dissolved in about 100 cc. of benzene in a small flask provided with a condensing-tube. About four grams of aluminum chloride in

small pieces were added, and the solution warmed gently. Solution began slowly with the evolution of hydrochloric acid from the surface of the chlorides. The solution began to darken quickly, so after heating for five minutes the action was stopped by cooling the flask, and the contents were poured into half a litre of cold water, containing twenty cubic centimeters of concentrated hydrochloric acid. The manganese solution was then separated from the water, and evaporated to dryness.

The residue left after evaporating off the benzene was dark brown, tarry matter — some treated in different portions with alcohol, ether, chloroform and benzene, and the solutions filtered. Crystals separated from each of the solutions on evaporation, but the ether and alcohol dissolved less of the dark tarry substances, and consequently furnished the best crystals.

It was found on further experimenting that the chloroform solution yielded more satisfactorily when powdered, and therefore was

not necessary to use such a large proportion of benzene. The decomposition which takes place rapidly after the action begins could not be prevented, and it was found to have less effect on the final product than at first supposed it would.

Previously to using the method finally adopted the yield was small, — only six grams of the sulphone being obtained from thirty-five grams of the chloride. This method is similar to that used by Bedwell and Otto.[1]

[1] Ber. d. chem. Ges. 11, 2061

preparing formaldehyde-sulphoxylate from benzene sulphonic chloride and taking advantage of Hewitt's method for the removal of the chlorine from para-toluenesulphonic chloride and benzene. Only twenty grams of the chloride were used at a time, as this was found to be the largest convenient amount to handle. It was dissolved in an equal weight of benzene in a flask provided with a condensing tube. The solution was placed in a water-bath, and heated so that the benzene solution boiled gently. Fifteen grams

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of freshly prepared ammonium chloride were added gradually — three or four grams at a time — allowing the mixture to be boiled after each addition. The solution was heated for a half an hour, then allowed to cool, and poured into a litre of water containing twenty cc. thirty cubic centimeters of concentrated hydrochloric acid. A voluminous bright brown, gelatinous precipitate formed. The solution was removed on the water-suction, all of the liquid was drawn off; the precipitate pressed off, and drained

with the filter-pump. The precipitate was repeated until two thousand grains of the chloride had been used, from which were obtained two thousand and forty-four grains of the dry, metallic product. Most of it was found to be soluble in alcohol, but the yield was considerably decreased in the process of purification.

The collected residues were extracted with hot alcohol, and the alcoholic solution boiled with animal charcoal until nearly colorless, and filtered while hot with the aid of a hot water-funnel.

The unmarked difference in the solubility of the sulphone in hot and cold alcohol caused considerable difficulty in its purification. Most of it crystallized out from the alcohol on cooling in the form of thin silver-white plates melting at 125°C. (corr.) That which remained dissolved in the cold alcohol was obtained by concentration of the solution. This part of the product was not as pure as that which first separated out from the solution, as it was found that on steam distillation of the sulphone it became brown and

for a while, or even allowed to stand over night. The charcoal took up a considerable amount of the sulfobrom, which was recovered by extracting with alcohol.

Analysis of the product gave the following results, -

I. 0.3140 grams gave 0.2032 grams $BaSO_4$

II. 0.1518 grams gave 0.1010 grams $BaSO_4$

III. 0.2863 grams gave 0.5934 grams CO_2 and 0.1058 grams H_2O

IV 0.2994 grams gave 0.6201 grams CO_2 and 0.1053 grams H_2O

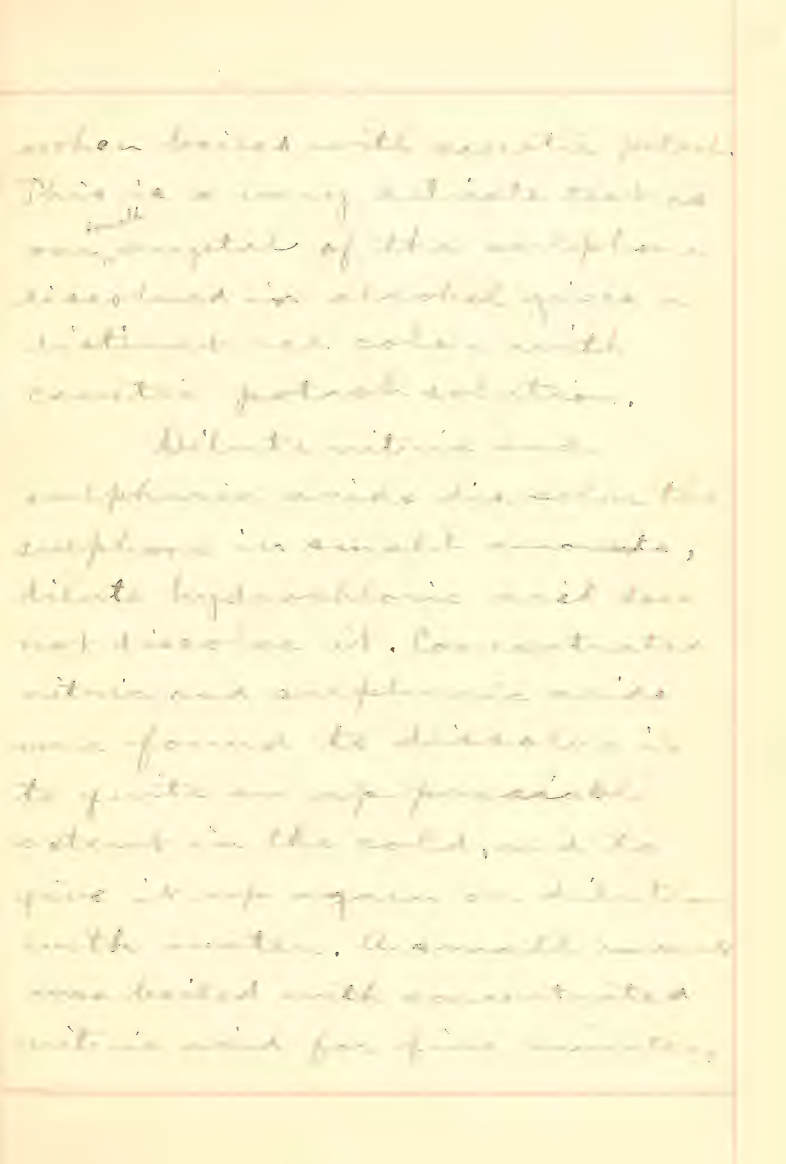
V 0.3229 grams gave 0.017 grams N.

	Calculated[1] for $C_{13}H_{11}O_4NS$	I.	II.	III.	IV.	V.
C	56.30	----	----	56.5%	56.52	----
H	4.00	----	----	4.13	3.93	----
S	11.56	11.60	11.76	----	----	
N	5.06	----	----	----	----	5.26

Paranitroorthotolylpheny-
sulphone exhibits in a marked
degree the general stability
of sulphones toward
concentrated acids. It is,
however, much less stable
toward alkalies than the
simpler sulphones, probably
on account of the presence
of the nitro group. Most of
the ordinary organic
solvents dissolve it readily.

[1] All calculations from analytical results are made by the use of the atomic weights published by Clarke, Jour. Am. Chem. Soc. 19, 848.

It was found to be readily as soluble in nitrobenzol as in ethyl alcohol. Benzene and toluene dissolve it very readily, and it is deposited from the former in the form of plates and from the latter as needles. It was almost equally soluble in hot and cold ether, and to a rather small extent. Hot ligroin dissolved it with ease, but on cooling it is practically insoluble, even when the mixture is boiled; but that it does dissolve to a ——— extent is shown by the fact that the filtrate from a concentrated solution gives a faint yellow



and united with water. The anhydrous acid precipitated as crystalline flocks and melted sharply at 122°C., showing that it had not been wetted appreciably by the acid. A similar experiment was performed with fuming nitric acid, with the same result. A mixture of equal parts by volume of concentrated nitric and sulphuric acids was then tried; this mixture which congeals at 0° and has a sharp melting-point. When boiled with a mixture of concentrated sulphuric and fuming nitric acids it was slightly decomposed. The

were not apparent at first, but the white precipitate which formed on dilution did not melt sharply.

The sulphone dissolves quite readily in ordinary concentrated sulphuric acid to the extent of 10 per cent. and is precipitated unchanged when the solution is poured into water. When the acid was warmed to 100° C. the solubility of the sulphone increased, but it was not acted upon. When the temperature was raised much above this the sulphone was decomposed or charred by the charring. Fuming

[illegible] sulphonic acid and
the [illegible] sulphonic acid,
it was not precipitated
on dilution.

Action of Fuming
Sulphuric Acid on
Paranitrobenzol Sulphonic Acid.

A small amount of the
sulphonic was treated with
fuming sulphuric acid
in a test-tube, and heated
quickly for four or five
minutes until it got to
100° C. After cooling, it was
poured into a small
amount of water. No precipi-
tate formed, but upon the
addition of more water, it
[illegible]

vaseline on the bottom
plate. The precipitate
would not, therefore, have
been the same as would
be obtained if the solution
were contained
many of which would have
been precipitated on the plate.
The sulphuric acid bath
completely saturated with
arsenic sulphide.

The experiment was
repeated on a larger scale.
The grooves of the sulphuric
treated with about forty grams
of pure arsenic sulphide and in
a small beaker, with which was
placed on a water bath, and
heated to 100° for half an
hour, the solution to the

was poured into half a
litre of water. No precipitate
formed. Barium carbonate
was added to the solution
till it ceased to cause
effervescence. During the
digestion of the sulphate
with soda the solution became
dark brown, and it increased
in intensity during the
heating. This colour appeared
again on the barium salt, so
it was necessary to treat it
with a little of charcoal. After
this the solution was allowed
to cool, and the barium salt
crystallized out as needles.
The analysis of the barium salt
gave the following results,

0.0849 grams lost 0.0097 grams at 150° C.
0.0752 grams of the anhydrous salt
gave 0.0209 grams $BaSO_4$.

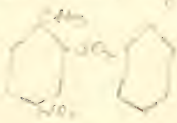
	Calculated for	Found.
	$(C_{13}H_{10}O_7S_2N)_2Ba + 6H_2O$	
H_2O	11.28	11.42
	$(C_{13}H_{10}O_7S_2N)_2Ba$	
Ba	16.16	16.35

Paranitroorthotolylphenylsulphone
sulphonic Acid.

The acid was obtained from
the barium salt by treating
a solution of the latter with
just sufficient sulphuric acid
to precipitate the barium as
barium sulphate, and filtering.
It was found to be readily
soluble in water, and crystal-

ized from the solution in the form of very fine white needles. They were readily soluble in alcohol, but difficultly in ether and benzene.

From analogy to the sulphonic acid formed from phenylsulphone,[1] and from the fact that three of the positions in one of the benzene rings are already substituted, it seems probable that the sulphonic acid residue enters the phenyl group of the sulphone in the meta position, forming a compound of the formula,



① Otto and Knoll, Ber. d. chem. Ges., 11, 2075
Otto, Ber. d. chem. Ges., 19, 2417

Action of Potassium Hydroxide on Paranitrobenzaldehydephenylsulphone.

A warm benzol solution of paranitrobenzaldehydephenylsulphone was added to a solution of potassium hydroxide in absolute alcohol. A deep purple color was developed immediately. The solution was warmed on the water bath for a few minutes, and finally a purple colored precipitate formed. This was separated by filtering, washed with benzol, water and

sulphuric acids were added to different portions of the solution. They changed the color to reddish yellow, which was changed back again to purple on addition of excess of potassium hydrate. The basic solution was neutralized again by the addition of either ammonium sulphate or sodium carbonate to the acid solution. Concentrated sulphuric, nitric, and hydrochloric acids produced apparently the same effect as the dilute acids. But when the solutions were made neutral again with caustic potash the

purple color did not return. The purple colored compound was completely decomposed by the hydrochloric acid.

Potassium was found to have no effect on the sulphide as a solution in alcohol. Ammonium hydroxide and sodium carbonate had no action on the sulphide.

An attempt was made to isolate the compound formed. About four grams of the sulphide were dissolved in absolute alcohol, and treated with an alcoholic solution of pure potassium hydroxide. The solution was boiled for five minutes, cooled and poured

into about a litre of water. A red flocculent precipitate settled to the bottom of the vessel, leaving the supernatant liquid clear and not very deeply colored. The precipitate was washed by decantation until no longer alkaline, then boiled with water and washed again. After filtering off and drying, its solubility in a number of solvents was tested, for the purpose of purifying it. Treated with alcohol, ether, acetone and acetic acid it gave a slight red color to each, but did not dissolve appreciably. Evaporation of the solutions in each case left

Action of Reducing Agents on Para-nitrobenzoyl-phenylsulphone.

Observations on Sulphones.

Baeyer[1] found that nitrophenylsulphone was reduced with zinc and hydrochloric acid to amidophenylsulphone.[2] The yield is very poor, but the amidophenylsulphonic acid is easily reduced by the above reagent to form amidophenylsulphone.

The action of these reducing agents on para-nitrobenzoyl-phenylsulphone was also found to be remarkably

[1] Ann. Chem. (Liebig), 100, 208.

[2] Am. Chem. Jour. 8, 167

converted into an amide of uric acid in the animal economy.

Paracresotinic acid from tolyl phenyl sulphone.

Four grams of paratoluene tolyl phenyl sulphone were dissolved in 100 c.c. of hot alcohol, about 20 c.c. of concentrated ammonia water added, and sulphuretted hydrogen passed into the solution for fifteen minutes. The solution became blood-red in color, which intensified considerably on warming. After this sulphuretted hydrogen had been passed into the solution ammonium sulphide could be made to crystallize out on cooling, whereas if care was not taken the original solution readily on a slight [illegible]

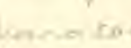
of the temperature. A small amount of the solution was removed and treated with water, which caused a voluminous precipitate of white needle shaped crystals to form. The main portion of the solution was then evaporated to dryness on a water-bath, and the residue digested with water. Sulphuric acid was added to the solution remaining undissolved, which consisted of sulphur, was removed by filtration through glass wool and the filtrate alkaline with caustic soda a heavy white precipitate

same manner. This was filtered off, washed and dried with the filter pump. It was then dissolved in alcohol, treated with animal charcoal, boiled, filtered and allowed to crystallize out. The crystals were long, hexagonal shaped, colorless plates, and melted at 178° C. (uncor.). They were difficultly soluble in cold water, and crystallized out from this solution in very small plates. Alcohol and acetone dissolved them readily, and they were precipitated from either solution on addition of water. They dissolved in dilute acids and in alkalies

void one hour at the ... Evaporation
[illegible] ... crystalline
... the compound crystallized
out in the form of needles.

Determination of nitrogen
gave the following results, —
0.1621 grams gave 17.5 c.c. N at 17° C. and
765 mm. Hg. pressure = 0.0171 grams.
0.3496 grams gave 37.5 c.c. N at 18° C.
and 765 mm. Hg. pressure = 0.0399 grams.

	Calculated for $C_{13}H_{13}O_2NS$	Found.	
N.	5.6 %	5.5 %	5.6 %

From its formula, 
it appears that this compound is
a derivative of paratoluidine.
It is such it readily forms
salts with inorganic acids

Action of Oxidizing Agents on Paranitrorthotolylphenylsulphone.

Chromic Acid.

Nawalᵃ found that the best method for converting paratolylphenylsulphone into parasulphonebenzoic acid was by treatment with chromic acid in glacial acetic acid solution. The same method was tried with this sulphone.

The grains of the sulphone were dissolved in glacial acetic acid and added to boiling in a flask attached to an inverted condenser. It

ᵃ Loc. cit.

saturated solution of about
twelve grams of chromic
acid in glacial acetic acid
was added in small
quantities at a time, the
solution being kept just
hot enough to boil gently.
After all the chromic acid
was added the solution
was boiled for three hours.
The solution was filtered,
and the acetic acid evapo-
rated off from the filtrate.
The original precipitate was
found to consist of chromic
oxide, Cr_2O_3, almost free
from organic matter. The
residue from the filtrate
consisted principally of

sensitized sulphonal mixed with the chromic acid test remained.

Repetition of the experiment gave the same result.

The action of chromic acid in this case, or rather its lack of action is in accord with its general behavior towards orthocarbinol ketones, products of ketones. The presence of the phenylsulphone group, $(SO_2C_6H_5)$, in the ortho position to the methyl group seems to shield it from the action of chromic acid.

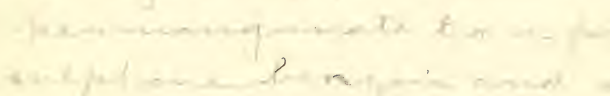
Potassium Permanganate.

The most efficient oxidizing agent for arithmetical titrations is, beyond question, that generally known as potassium permanganate in water solution.

The action of oxidizing agents on sulphites was first investigated by R. Otto.[1] He found that when pure sulphite was mixed with water acidified with sulphuric acid and titrated with potassium permanganate, the permanganate was converted instantly, or almost so, by the precipitation of manganese dioxide. Mohr

[1] Ann. Chem. (Liebig) 1845, 37.

and Ortner,[1] obtained by
the action of phenylhydrazine
on ethyl phenylglyoxylate
ethyl phenylhydrazone was
oxidized by potassium
permanganate to an
acid and to a
phenylsulphonedabbinpic acid
respectively;—



When the action was carried
on in acetic acid solution the
yield was small. A water
solution of potassium
permanganate oxidized
both, readily, at the
sulphone group
oxidized in water and

[1] Ber. d. chem. Ges., 11, 119.

half of it was oxidized by the theoretical quantity of potassium permanganate.

Paramethoxytolylphenyl sulphone was found to act in a similar manner.

Marcusson and Stangl[1] have determined by experiment that one molecule of potassium permanganate gives up two and a half atoms of its oxygen to an oxidizable substance and reduces the free mineral acid in the mixture. It would therefore require three molecules of the permanganate to oxidize the sulphones if all of the oxygen liberated were used in

[1] Jour. Prak. Chem. 126, 78

oxidizing method for removal. It was found, however, that a much longer oxidation was required. This is to be accounted for partly by the fact that the sulphone is probably completely broken down to a certain extent into higher oxidation-products[1], and also that the manganese dioxide first formed itself decomposes the potassium permanganate[2] somewhat.

① R. Otto Loc. cit.

② Morse, Hopkins and Walker, Am. Chem. Journ. 13, 401

Preparation of Naphthalene-1-sulphonic acid.

The acid was prepared by the following method:

Sixty grams of the sulphonic were prepared in about a liter of water in a flask. The sulphonic acid was previously powdered and as fine as could possibly be obtained in a mortar. A solution of thirty grams of potassium permanganate was added, one quarter at a time, at intervals of an hour, the solution being heated to boiling meanwhile on a sand-bath. The color of the permanganate was gradually

disappeared by the time the manganese dioxide in the reaction progressed. It was difficult to determine from the appearance of the solution when the last trace of the permanganate had disappeared, without halting the solution with, which required considerable time. Samples were removed intermittently and filtered, and portions of colorless filtrate were withdrawn with a pipet. The reaction was stopped. By measuring required exact amount to decolorize all of the potassium permanganate. The solution was allowed to settle over

night, and then the clear supernatant liquid decanted off through a filter. On acidifying the filtrate with hydrochloric acid a white, finely divided precipitate came down, which aggregated into irregular, needle-shaped crystals on standing. This was filtered off and purified by redissolving in water, which usually left some of the sulphur undissolved, and treating with animal charcoal. The largest yield of acid obtained from 10 grams of the sulphone was 7.5 grams. A considerable amount of sulphone was always left unacted upon and

prepared yield the corresponding disulfide principals. It was recovered by dissolving the dioxide in dry benzene, warming and filtering off the undissolved sulfone, which was not attacked by the reagent chloramine. Otto[1] found that phenylsulfonacetic acid is not attacked by aqueous chloramine in solution, but on the other hand that dry chloramine acts on the sulfone at its melting point in diffused light to form benzenesulfonchloramide and monochlorbenzene.[2]

[1] R. Otto, Loc. cit.

[2] Otto, Ann. Chem. (Liebig), 141, 93

Paramitroanthraquinone sulphonic acid forms crystallizes in white needles 5 to 10 mm. long, melting at 1½° C. (uncor.). It is difficultly soluble in cold water, and not at all readily in hot water. It has a bitter taste. Reducing dissolves it readily, but ether and benzene only to a small extent.

Salts of Fremy's methylene disulfonamidosulfonic acid.

Barium methylene disulfonamidosulfonate, $CH_2(NH.SO_2.NH.SO_2.NH_2)_2.Ba.H_2O$, was obtained by dissolving barium carbonate in a solution of the acid. It crystallizes in the form of short, white needles, usually united together, and difficultly soluble in hot water. Analysis gave the following results:—

I. 0.3784 grams lost 0.0100 grams at 175° C. and gave 0.1146 grams $BaSO_4$.

II. 0.5043 grams lost 0.0125 grams at 175° C. and gave 0.1524 grams $BaSO_4$.

Calculated for	Found.	
$(C_{13}H_8O_6NS)_2Ba.H_2O$	I	II
H_2O 2.34	2.64	2.48
$(C_{13}H_8O_6NS)_2Ba$		
Ba. 19.22	19.36	19.40

Calcium nitrophenylsulphonic benzoate ($C_6H_3NO_2SO_3C_6H_3CO_2)_2Ca.2H_2O$) was obtained by heating a solution of the acid with an excess of barium. It crystallizes in tufts of needles, colorless, prismatic crystals, readily soluble in hot water.

Analysis of the salt gave the following results, -

0.1104 grams lost 0.0292 grams at 110°C.

0.1812 grams lost 0.0343 grams at 110°C.

Calculation for

$(C_{13}H_8O_6NS)_2Ca.6\frac{1}{2}H_2O$

$6\frac{1}{2}H_2O$ 15.21

$(C_{13}H_8O_6NS)_2Ca.$

Ca 6.14

Comparison of Paramitra-orthoplemplan-phenanthrenephenanthridine with Para-tri-ortho-benzoyldibenzophenanthridine.

Mathis[1] found that the acid formed by the action of water and dilute acids on the product of the Friedel and Crafts reaction with the chlorides of paramitrotoluene-sulphonyl chloride, was very easily soluble in water, and could not be obtained in a crystallized form. It forms with crystallized salts with varying amounts of water of crystallization, but none less than three molecules.

[1] Loc. cit.

The magnesium salt of the half of carboxylic acid is a monomolecular film. The calcium salt is crystallized in thin plates with three molecules of water of crystallization.

Para-nitrobenzoylphenylglycine-ortho-carboxylic acid, on the other hand, is rather difficultly soluble in water, and crystallizes readily. The barium salt crystallizes in short needles united together, containing two molecules of water of crystallization. And the calcium salt crystallizes in prisms containing 3½ and in leaf molecules of

waters of crystallization.

The differences may be brought out more strikingly by means of a table,

Paranitrobenzoic acid.	Parahydroxybenzoic acid.
Very soluble in water.	Difficultly soluble in water.
Not crystallizable.	Crystallizes easily.
Benzene and carbonic disulphide dissolve traces of water of crystallization,	Benzene and carbonic disulphide dissolve traces of water of crystallization, and crystallize.

and respectively in terms of mediating vessels, or mesenchymal primordia.

Calcium salts respectively in plants with three molecules of acetone of respectively.

should respectively mentioned together.

Calcium salts respectively in primordia with one and a half molecules of water of respectively.

Action of Phosphorus Pentachloride on Phenyl-o-nitrophenylsulphamic Acid.

Phosphorus pentachloride acts readily on the free acid to form phenylnitrosulphamyl sulphonic acid chloride.

When the acid was intimately mixed with phosphorus pentachloride & the mixture heated in a paraffin bath until the temperature was raised to 110°C. Dark red fumes of phosphorus oxychloride & hydrochloric acid began immediately at the ordinary temperature on

mixing the two together.

The reaction which takes place may be represented thus:

Paranitrocresotinophenylsulphonic Chloride.

Equal weights of paranitrocresotinophenylsulphonic acid and phosphorus pentachloride containing a small amount of the oxychloride were intimately mixed in a mortar. The mixture gradually softens and enters in to liquefaction, with evolution of hydrochloric acid

[illegible] of [illegible]
[illegible] and phosphorus
oxychloride. After the action
was over the mass was
transferred to an evaporating
dish and heated for ten
minutes longer, to about 110°C.
It then had the appearance
of a light brown liquid.
This was allowed to cool to the
ordinary temperature, and
washed with cold water, which
removed it to solidify to a
yellow granular solid. It
was powdered up to a fine
powder and washed with
fresh portions of water,
dried with filtering-paper, and
[illegible] in vacuum over chloroform

It crystallized out of the solution on the spontaneous evaporation of the chloroform as well-formed, colorless, rhombic crystals from one to five millimeters long, having a melting-point of 104° C. (uncorr.) The crystals were easily soluble in chloroform, ether, benzene and ligroïn.

Chlorine was determined in the chlorinde by heating with a dilute solution of sodium carbonate made up from metallic sodium, acidifying with nitric acid and precipitating with silver nitrate.

I. 0.1631 grams gave 0.0716 grams AgCl.
II 0.1847 grams gave 0.0810 grams AgCl.

	Calculated for $C_{13}H_8O_5NSCl$	Found I.	Found II.
Cl	10.88	10.85	10.84

Action of Water on Paranitrobenzoylphenylsulfonyl Mercuric Chloride.

The chloride is quite stable toward water at ordinary temperatures. No change could be detected in a fine crystalline specimen in contact with water several days. Heat it is readily decomposed when boiled with water.

Nitric reagents also act on

solution decomposes the chloride much more quickly than water. Two-tenths of a gram of the chloride was entirely decomposed and passed into solution when boiled with a very dilute solution of caustic potash for five minutes. Hydrochloric acid was added to the solution in excess, and many fine needle-shaped crystals separated out on cooling. Their melting-point, 146° C., showed them to be *para*-nitrobenzoic acid. The reaction with water may be represented thus:—

$$C_6H_4\begin{cases}COCl\\NO_2\end{cases}(1,4) + H_2O = C_6H_4\begin{cases}COOH\\NO_2\end{cases}(1,4) + HCl.$$

Action of Ammonia on Some Known Chlorides of Benzoyl Chloride.

By the action of ammonia the chlorine of the benzoyl chloride group is replaced by the amido residue.

Some of the benzoyl chloride was added to a dilute solution of ammonia in a flask and allowed to remain in contact with it several days. The residue left at the end of this time had the same appearance as the chloride - a light yellow powder. The ammonia was evaporated off on a water bath, and the solution filtered from the

residue crystallized from alcohol and dissolved in hot chloroform, in which it is readily soluble. It crystallized out on spontaneous evaporation of the chloroform in well-formed, colorless, prismatic crystals, apparently monoclinic, and melting at 191°–192° C. (uncor.) The crystals were analyzed with the following results,—

I. 0.4049 grams gave 0.3004 grams $BaSO_4$.

II. 0.1515 grams gave 0.2310 grams $BaSO_4$.

	Calculated for $C_{13}H_{10}O_5N_2S$	Found I	Found II
S	10.46	10.19	----
N	9.16	----	9.14.

The reaction, therefore, which takes place is,

$$C_6H_3 \begin{cases} 2\,OH \\ 1\,NO_2 \\ 2\,CO_2H \end{cases} + 2\,NH_3 = C_6H_3 \begin{cases} 2\,OH \\ 1\,NO_2 \\ 2\,CO.NH_2 \end{cases} + 2\,H_2O$$

The reaction being the formation of

Para-nitrotetraphenyldihydroxy-diamide.

The amide is practically insoluble in water, benzene, and ether, but dissolves readily in hot alcohol, and crystallizes out on the addition of water, in the form of prisms. Acetone also dissolves it very readily, and small flakes of pure amide crystallize out on evaporation of the acetone.

Action of Benzene and Aluminium Chloride on Paranitrotoluenesulphonyl Chloride.

On adding aluminium chloride to a warm solution of the orthonitrotoluenesulphonyl chloride in benzene a slight evolution of hydrochloric acid took place, and a brown tarry mass was obtained from which very little in the benzene could be extracted. Around the aluminium chloride and granular portion existed.

Two grams of the chloride were dissolved in about ten grams of benzene and two

grams of powder and chromium chloride added. The vessel was heated on a water-bath until the benzene began to boil. Hydrochloric acid was given off quite vigorously and fumed from the condensing-tube that was attached to the flask. The heating was continued for one hour. After the evolution of hydrochloric acid had ceased, the solution was cooled and poured into water. The water solution was washed with benzene and ether. The ether solution was dried over calcium chloride and the ether evaporated. The heavy residue solidified on standing

of the matter of the earth, was found to be insoluble in hydrochloric, nitric, citric, tartaric or acetic acids. It did not therefore seem worth while to further investigate.

Lack of material prevented the prosecution of many more experiments of this kind.

See the Friedel and Crafts reaction among many substances seems to suppress it, but this must be determined experimentally for each case. Then for the reaction the removal of the above group by experiment can be considered

condition as to whether the reaction expressed by the equation

may not take place under certain conditions.

Comparison of formation of the phenylazo derivative with that of benzoylbenzoylphenylhydrazine.

The compound obtained by Wolff[1] from the action of benzoyl and chloroacetic chlorides on the monochloride of phenylhydrazine, benzoylphenylhydrazine, separates from its solution in benzene

[1] Ann. ccxi

in the form of fine white crystals, sublimable in vacuum, melting at 177° C. It yields a water-soluble acid by the action of dilute hydrochloric and sulphuric acids out of contact of water, and when treated with concentrated sulphuric acid, with the loss of hydrochloric acid and water, to form a product which melts at 238°, and is almost entirely soluble in alcohol. The reactions, therefore, are in accordance with which would appear from the formulæ, $C_6H_5 \left\{ \begin{matrix} CO_2H \\ CO_2H \\ NH_2 \end{matrix} \right.$ and $C_6H_3 \left\{ \begin{matrix} CO_2H \\ CO_2H \\ NH_2 \end{matrix} \right.$

The constitution of phthamic acid

sulfur chloride, and
decomposes with the above
compound, crystallizes from
benzene in rectangular light
yellow rhombic crystals
melting at 109°C. It forms a
crystalline acid, when
boiled with water, which melts
at 142°C.; on the contrary with
ammonia it forms an insoluble
crystalline powder
which melts at 191°C to 192°C.
Other properties observations
do not quite distinct from the
compound of the above
empirical composition
obtained by Hantzsch.

An Attempt to Transform Paramitrotoluene-sulphonic Acid into Paranitrobenzoic Acid.

The unsuccessful attempt of paranitrotoluenesulphonic acid is converted into the corresponding salt of paranitrobenzoic sulphonic acid, $C_6H_4(NO_2)SO_3H$, under treatment with permanganate. It was thought that this substance might furnish the starting-point for another method for the preparation of paranitrobenzoic acid. But the action of potassium permanganate under the

[illegible] acid of the [illegible] formula, [illegible] nitrogen sulphur chloride, $C_6H_3\begin{cases}CN\\SO_2Cl\\NO_2\end{cases}$, is formed. It was hoped that by the action of benzene and chlorosulphonic chloride the desired sulphonyl chloride would be formed according to the reaction

$$C_6H_3\begin{cases}CN\\NO_2\end{cases} + C_6H_6 \rightarrow C_6H_3\begin{cases}CN\\SO_2C_6H_5\\NO_2\end{cases}$$

which by hydrolysis of the cyano group would give the desired sulphonic acid, -

$$C_6H_3\begin{cases}CN\\SO_2C_6H_5\\NO_2\end{cases} \rightarrow C_6H_3\begin{cases}COOH\\SO_2C_6H_5\\NO_2\end{cases}$$

The work carried out in connection with this investigation was performed by Miss A. E. Hendrickson of

(1) Gray, Inaugural Diss. Johns Hopkins University, p. 10 (1917)

this laboratory. The
recrystallized product
was obtained as a crystalline
product in the preparation
of the argentammonium chloride
of permanganic acid, was converted
into the potassium salt by
adding excess potash or
potassium chloride to its
solution in hot water. The
potassium salt is difficultly
soluble in cold water, and it
separates out as the solution
cools in the form of crystals.
Potassium chloride was found
to work more satisfactorily
than potassium hydrate. The
salt was boiled twice or three

Cy. Large, well formed,
pure and transparent prismatic
crystals were obtained which
melted at 104°.5 — 105°.5 C. (uncorr.).

The process of the estimation
was carried out as in the case of
cocaine hydrochloride, using 0.1
grams of powdered cinchonine
chloride added gradually
to a mixture of 10 c.c. water
and 10 c.c. ether. The
ether solution was then
collected in the bottom
forming a neutral emulsion with
the aqueous solution. The
solution was heated on the water

hydrochloric acid, and
extracted with chloroform.
The portion which remained
undissolved was the chloride
which is known, and is
formed insoluble in other
chloroform, benzene, and
carbon disulfide. The
chloroform extract was evaporated
to dryness on the water bath,
leaving a brown tarry mass
from which was obtained
a product which was shown
to be identical in all
chloroform, benzene and
carbon disulfide to that
in the above form as compared
of the solutions.

Conclusions.

The results of this investigation lead to the following conclusions, —

1. Paramitrotoluol phenylsulphone can be readily obtained by the action of benzene and chlorsulphonic chloride on paramitrotoluol-sulphone chloride.
2. This sulphone has the general properties of aromatic sulphones, and certain special properties due to the presence of the nitro-group.
3. Paramitrotoluol phenylsulphone is oxidized by potassium permanganate

an acetal solution to
para-nitrophenylsulphon-
ic-acid, and this would
be quite different in
properties from the isomeric
compound obtained by
decomposing the product of
the action of benzene and
chlorsulphonic chloride on the
chloride of para-nitrobenzene
sulphonic acid with
water.

4. Para-nitrophenyl
sulphonic acid and para-
nitrophenylsulphonic chloride
are quantitatively converted
into para-nitrophenyl
sulphamic acid when
treated with phosphorus
pentachloride.

5. Paranitroorthotoluenylenediamin
dinazoxylchloride has
perfectly definite properties
which distinguish it from
the isomeric substances
obtained by the action of
benzoyl and chloride
chloride on the chlorides
of paranitroorthotoluylene
diamin, especially the
formation of an amide by the
action of ammonia, while
the latter forms a basic

Biographical.

Robert Stewart Howie was born in Belleville, Ks., January 19, 1869. He received his primary education in the public schools of Topeka, Kansas, and prepared for college in the academic department of Washburn College at the same place. In 1887 he removed to Los Angeles, California, and entered the University of California in 1888, graduating in 1892 with the degree of B.S. He remained at the same institution as assistant in Chemistry for three years, and entered Johns

Hopkins University in 1877
where he have since pursued
courses in elementary
general biology, and
physiology. He was
appointed University
Scholar during the present
year.

Baltimore
May 1877.